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Nucleation of H_2SO_4 and Oxidized Organics in CLOUD experiment

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Abstract. The research of atmospheric new particle formation has proceeded lately as the role of sulphuric acid has been established. Still, the roles of other atmospheric compounds in nucleation remain largely unclear. To clarify the first steps of atmospheric new particle formation extensive nucleation experiments were performed in CLOUD chamber in 2012. Especially the role of oxidations products of α-pinene was studied in detail. The experiments provided new information about the part of oxidized organics in nucleation.
Keywords: nucleation, chamber measurements, atmospheric aerosols
PACS: 82.60.Nh, 82.33.Tb, 92.60.Mt

INTRODUCTION

Detailed steps of atmospheric new particle nucleation have been under debate and subject to numerous experimental and theoretical studies for decades. Despite the serious efforts, the exact molecular steps of nucleation remain unknown, though recent advances in mass-spectrometry[1,2,3] and particle counting technologies[4,5] are finally pointing toward a breakthrough. Sulphuric acid, H_2SO_4, has an established role in atmospheric nucleation[5,6,7,8] but sulphuric acid alone, or with water, cannot account for the high nucleation rates observed in the boundary layer[9]. Therefore, it has been suggested that additional vapours including bases – such as ammonia[9] or amines[10,11,12] – or oxidized organics[13,14] nucleate together with sulphuric acid and help the formation of new particles. Besides ternary vapours, it has been demonstrated that ions, produced in the atmosphere by galactic cosmic radiation and radon decay, can enhance the nucleation rate of new particles at least in sulphuric acid - water - ammonia system[9] potentially connecting the fluctuations of cosmic radiation to cloudiness and climate variations[15]. Some atmospheric observations, however, suggest that such a connection is weak or non-existent[16]. Here we report on our findings on the role of oxidized organics in neutral and ion-induced sulphuric acid nucleation in absence and in presence of ammonia and dimethyl amine.

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METHODS

Experiments were performed at CLOUD facility[9] in CERN during the CLOUD 7 run in autumn 2012. In the experiments α-pinene – a monoterpene, representative especially for boreal forests – was oxidized either with OH only or ozone only or with concurrent presence of both oxidants. Experiments were performed either in presence or in absence of ions in the chamber. Ions were produced in the CLOUD chamber by natural galactic cosmic radiation or, at enhanced concentrations by using CERN proton synchrotron pion beam. In the neutral experiments the complete absence of ions was achieved by sweeping the ions out from the chamber by high electric field. Some of the experiments were done in presence of varying concentrations of dimethyl amine or ammonia.

Experiments utilized a suite of recently developed instruments tailored for the purposes of the nucleation studies. Instruments comprise especially a Chemical – Ionization – Atmospheric Pressure Interface Time of Flight mass spectrometer (CI-APi-TOF) developed for detection of gas phase sulphuric acid and nucleating sulphuric acid containing clusters, as well as oxidized organic reaction products[3], a Particle Size Magnifier[4] and other instrumentation (e.g. NAIS, DEG-CPC etc.) for detecting the particles immediately after their nucleation. Nucleation studies of sulphuric acid and amines in absence of α-pinene and its products are described elsewhere[17].

The CI-APi-TOF[3] relays on chemical ionization of sample molecules and clusters by nitrate ions. In the new version of the CI-APi-TOF, developed for the CLOUD 7 campaign, the primary ions are generated by irradiating nitric acid containing sheath flow by photons from a soft x-ray source. Main advantages of the x-ray source in comparison to Am-241 source used in original instrument[3] are that it is non-radioactive and can be switched on an off. Primary ions are then mixed with the sample flow by means of electric fields. CI-APi-TOF can be used for detection of strong acids and acidic clusters that can donate a proton to nitrate ion, as well as certain compound groups, including highly oxidized organics, which can form stable ionic clusters with nitrate ions.

RESULTS

The nucleation rates of experiments were calculated and the values were compared with the prevailing conditions. Especially the correlation with sulphuric acid and oxidized organics was studied in detail. The concentration of sulphuric acid and oxidized organics were calculated from the CI-APi-TOF data. The monomers of oxidized organics were considered to be organic compounds between mass charge values from 300 to 450. Figure 1 shows an example of particle formation in an experiment with α-pinene, SO_2 and dimethyl amine. The effects of different concentrations of oxidized organics and sulphuric acid on nucleation rates in presence and in absence of dimethyl amine or ammonia, were studied and the results will be discussed.

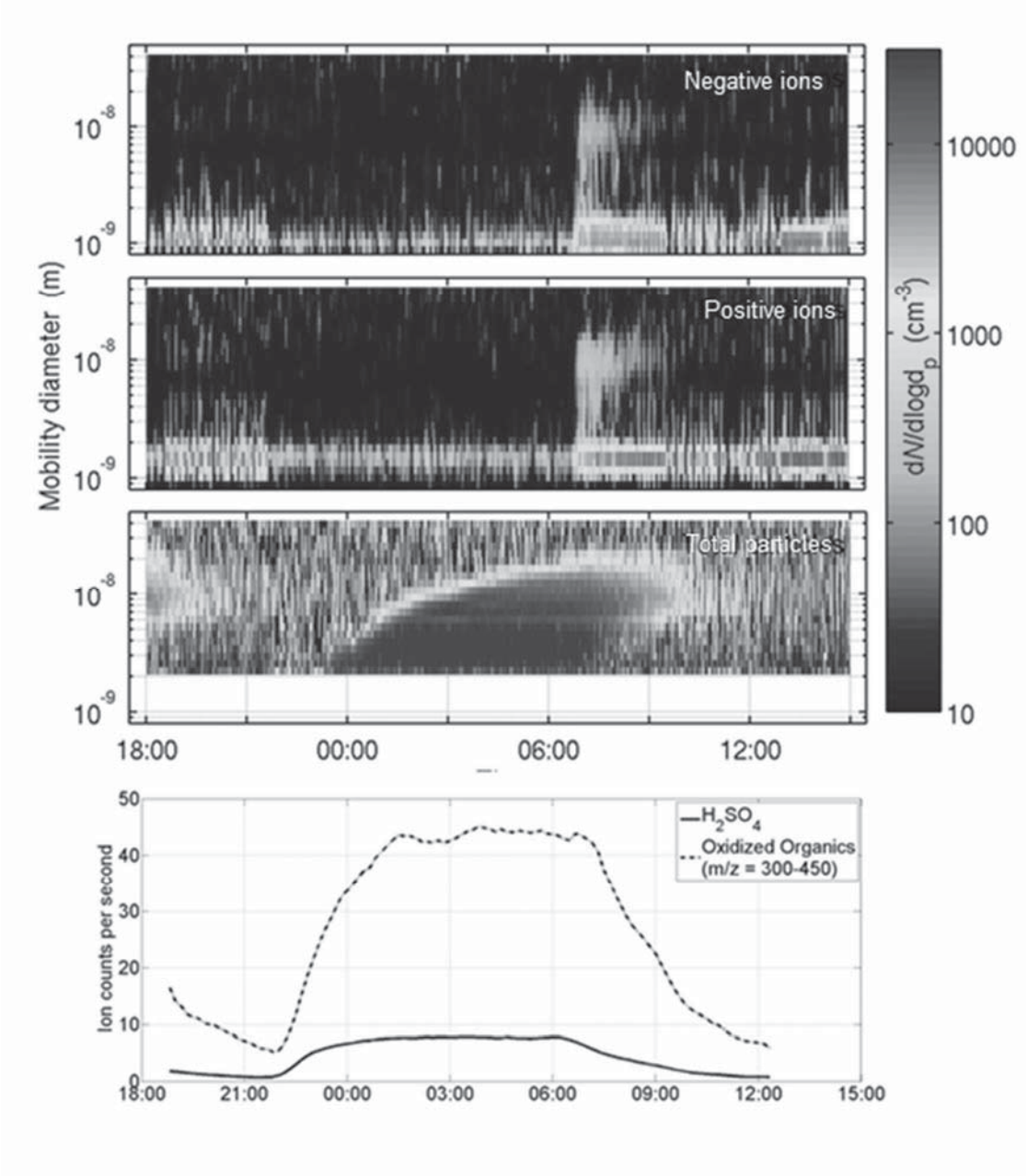

Figure 1. An example of the behaviour of particles measured by NAIS and sulphuric acid and oxidized organics monomers measured by CI-APi-TOF during an experiment where α-pinene and dimethyl amine was added into the chamber.

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